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V. YEFIMOV, T. PURRE

CHARACTERISTICS OF KUKERSITE OIL SHALE, SOME REGULARITIES AND FEATURES OF ITS RETORTING

Over the seventy years of commercial scale retorting of Baltic oil shale (kukersite) considerable studies have been carried out on its physical, chemical and technological properties. The results of these studies combined with operational experience have greatly contributed to further perfection of oil shale retorts now in operation in Estonia and in Leningrad district. However, no generalized evaluation of these data and experience has been published so far. It will therefore be of interest for further development of new retorts to discuss here some technological properties of kukersite characterizing it as a raw material for thermal processing.

One of the process design criteria is the yield of shale oil characterized by the Fischer assay test. Experience has shown that the Fischer-assay oil yield (T_{sK}^{d}, %) from kukersite is a function of its heat of combustion and can be quickly calculated according to the following equation [1]:

$$T_{sK}^{d} = 1.767 \cdot Q_{b}^{d} - 0.162$$

(statistically $r = 0.9999$ and the standard deviation $\tilde{s} = 0.129$), where Q_b^d is the calorimetric heat of combustion on a moisture-free basis, MJ/kg. It is interesting to note that practically the same equation is valid for Green River oil shale:

$$T_{sK}^{d} = 1.767 \cdot Q_{b}^{d} + 0.001 \qquad (r = 0.9999, \tilde{s} = 0.004)$$

One of the characteristics of kukersite causing considerable difficulties in its commercial scale processing is its bituminizing on slow heating — the transition to the plastic state within the temperature range 350—400 °C. The maximum yield of thermobitumen is produced at 390—395 °C and it makes up to 55—57 % of organic matter irrespective of oil shale quality. At these temperatures carbon content of the solid residue (remaining after extraction of thermobitumen with a mixture of ethanol-benzene) is of the minimum value. However, as the heating continues to 510—520 °C the carbon content of the residue increases 2—3-fold. In case of other shales the carbon content in semicoke reaches its minimum value only by the end of retorting [2].

This feature of kukersite can be most likely explained by the relatively high content of thermally unstable components like oxygen-containing compounds (including high-boiling phenols) in the volatiles. As a result most of the carbonaceous residue in semicoke is of secondary origin formed at the pyrolysis of these unstable compounds. The most widespread oil shales of the world typically form paraffin-rich oil on their retorting. The content of oxygen-containing compounds, including phenols, in these oils is negligible or they are absent altogether.

It follows from the characteristics of kukersite that its volatile products are

Yield and Properties of Raw Shale Oil Obtained on Processing Kukersite

Characterictics	Labora-tory Fischer retort (200 g)	Hori-zontal rotary retort	Tunnel ovens	Vertical direct heated retorts (gene-rators)	Processing oil shale in 500 t/day Galoter retort with solid heat carrier: temperature of heat carrier, °C		Processing oil shale in fluidized bed: Laboratory batch-type retort (500 g): Heat carrier gas		Processing oil shale in fluidized bed: Pilot plant (25 t/day)*
					765	850	N_2	CO_2	
Oil shale									
Moisture, %	0.56	8.0	9.0	8.7	11.8	12.0	1.8	1.87	7.3
Organic matter (dry basis), %	33.0	30.0	35.0	33.5	34.5	32.7	34.5	32.1	36.1
Calorific value (bomb calorimeter), MJ/kg	12.43	11.22	13.36	13.06	13.10	12.06	13.06	12.27	13.86
Shale oil									
Yield, %:									
on initial shale basis	21.2	16.5	20.8	16.4	13.5	14.4	19.9	19.4	-
on organic matter	65.5	59.8	65.3	53.6	44.5	50.1	58.8	61.7	-
Density at 20 °C, kg/m^3	968	949	965	1000	975	966	1036	1046	1099
Viscosity at 75 °C, 10^{-6} m^2/s	5.5	6.2	5.1	18.7	6.9	3.5	-	-	43.0
Flash point, °C	6	9	25	104	9	-	-	-	110
Initial boiling point, °C	66	64	65	170	80	68	-	-	210
Distillation (Vol. %):									
to 160 °C	15	15	9	-	13	19	-	-	-
180 °C	18	18	11	1	17	25	-	-	-
200 °C	21	22	14	2	21	30	-	-	-
220 °C	25	24	16	4	25	34	-	-	2

Table (continued)

Characterictics	Laboratory Fischer retort (200 g)	Horizontal rotary retort	Tunnel ovens	Vertical direct heated retorts (generators)	Processing oil shale in 500 t/day Galoter′ retort with solid heat carrier: Temperature of heat carrier, °C		Processing oil shale in fluidized bed		
							Laboratory batch-type retort (500 g): Heat carrier gas		Pilot plant (25 t/day)*
					765	850	N_2	CO_2	
240 °C	30	27	20	6	28	38	-	-	6
260 °C	35	30	24	8	32	41	-	-	11
280 °C	42	34	28	12	36	45	-	-	16
300 °C	56	39	35	19	41	50	-	-	-
320 °C	78	44	40	24	47	54	-	-	-
340 °C	-	53	-	35	56	60	-	-	-
360 °C	-	68	-	60	66	71	-	-	-
Phenolic compounds, %	19.4	23.1	22.3	28.1	15.0	10.9	29.5	33.2	-
Calorific value (bomb calorimeter), MJ/kg	40.19	40.11	40.11	40.00	39.82	40.19	39.85	38.31	37.89
Elemental composition, %:									
C	83.12	81.5	82.6	83.5	83.6	84.0	82.69	80.36	83.55
H	10.13	9.9	10.4	10.1	10.1	9.7	10.08	9.16	8.75
S	0.84	1.1	0.9	0.7	0.9	0.5	0.7	0.68	0.65
O + N	5.91	7.5	6.1	5.7	5.4	5.8	6.53	9.80	7.05
Molecular mass	276	-	276	287	300	296	302	299	455

* yield of oil not determined because of short run

thermally unstable at the moment of their formation and they undergo considerably more extensive secondary pyrolytic transformations as compared with other shales. Therefore in order to obtain the maximum yield of oil with an elevated content of phenols including water-soluble alkyl resorcinols it is of utmost importance to evacuate the volatile products of kukersite retorting from the reaction zone, particularly from the microporous structure of shale lumps without delay. The best way to obtain this is processing kukersite in a flow of gaseous heat carrier with a low partial pressure of oil vapours; the gas for heat carrier must be taken after it has passed the condensation system of the unit.

On retorting kukersite first of all the fine fractions rich in organic matter undergo bituminization. On retorting large particle oil shale troublesome consequences of bituminization — sticking of organic matter to the retort walls, formation of hangings, etc. could be eliminated by better screening out fine fractions from the feedstock and retorting oil shale in a thin layer — 1.0—1.5 m that enabled to pass the temperatures of maximal thermobitumen formation at a relatively high speed (not less than 3—4 °C/min). The best realization of these conditions was obtained in retorts with cross-current heat carrier flow. Switching to the retorts with cross-current heat carrier flow enabled at last to create retorts of high capacity for thermal processing of such a "difficult" feedstock as kukersite.

Another feature characterizing kukersite is the predominance of calcium carbonate in its mineral part. This compound dissociates at high temperatures forming free calcium oxide which absorbs phenols on contact with the volatile products. As a result the content of light fractions in total oil increases considerably while their utilization remains at present problematic. Therefore direct contact between volatile products and solid residue which contains free calcium oxide should be avoided on kukersite retorting. However, if light fractions could be utilized properly, the solid heat carrier units, for instance, contrary to other retorts, enable to obtain shale oil with an increased content of light fractions. Retorting oil shale at thermally severe parameters the share of gasoline fraction (boiling to 200 °C) in total oil (see the Table) can reach 30 vol. % with a phenols content as low as 10 % [3]. As seen from the Table, the physical and chemical properties of kukersite oil are greatly influenced by the presence of phenols, i.e. by the conditions of evacuation of volatile products from the reaction zone on retorting oil shale.

One must bear in mind that on thermal processing of large particle shale dissociation of carbonates is negligible; this process intensifies if oil shale is more degradated. The following equation is proposed for a quick estimation of the carbonate dissociation degree (ß, %) on thermal processing of kukersite:

$$\beta = 100 - 244 \cdot K_{CO_2}^{residual}$$

where $K_{CO_2}^{residual}$ expresses the ratio of $(CO_2)_M^d$ to A^d in the solid residue.

Owing to a considerable amount of thermally unstable compounds among volatile products formed during retorting, oil shale moisture favourably influences the kukersite retorting process enabling accelerated evacuation of volatiles from the pores of lump shale and increasing therefore the content of phenols in the oil. For that reason a preceding drying of kukersite is not practical as this may essentially (up to 20—30 relative %) lower the content of phenols and lead to lighter fractional composition of the oil.

It is known that the presence of oxygen in the retorting zone is of decisive importance in determining the yield of oil from processing kukersite [5, 6]. On retorting oil shale with gaseous heat carrier it is extremely important to minimize the absolute amount of oxygen entering the semicoking shaft [7]. At the present technological level of retorting process (with gasification of semicoke and combustion of gas in special burners) there exists an evident relationship between the oil yield of the Fischer assay (y, %) and the specific consumption of air in the process (x_0, m^3/t):

$$y = 98.3 - 0.056 \cdot x_0 \qquad (r = -0.9660,\ \tilde{s} = 3.4)$$

The negative effect of oxygen on the oil yield on retorting large particle shale is most likely caused by the oxidative pyrolysis of volatiles in semicoking shaft accompanied by their partial combustion. Therefore a direct relationship between specific yield of hydrogen on organic matter basis (x_1, m^3/t) characterizing the intensity of pyrolysis of volatiles in the semicoking shaft of a certain retort, and specific consumption of air in the process can also be observed [8]:

$$x_1 = 0.250 \cdot x_0 + 20.9 \qquad (r = 0.9130,\ \tilde{s} = 0.8)$$

The less oxygen enters the semicoking shaft the less secondary pyrolytic transformations of volatile products take place and the higher is the oil yield.

As for the essential effect of specific air consumption upon the process on retorting lump shale one has to bear in mind that contrary to other oil shales it is fairly difficult to obtain high oil yields from kukersite. It may be explained by the fact that on thermal processing of kukersite, unlike the oil shales of other deposits, its elevated moisture percentage and the predominance of calcium carbonate in its mineral part result in high values of specific heat consumption in the process (approximately twice as high as, for instance, in case of oil shales from Green River and Irati) [9]. That is why on thermal processing of kukersite the specific consumption of air must be kept at a high level which, however, decreases the oil yield. Therefore the reduction of specific heat consumption and, consequently, specific consumption of air in order to decrease the concentration of oxygen in the reaction zone has become one of the most actual problems in utilizing kukersite. The Oil Shale Research Institute and the Oil Shale Processing Association have developed a new retort design with a circular semicoking chamber to improve the distribution of heat carrier across the shale bed. It has already been demonstrated in practice, that in these units, as compared with the retorts presently in operation, the distribution of heat carrier across the shale bed has indeed improved resulting in a decrease of the temperature of oil vapours at the gas offtake from 200—250 °C to 140—160 °C and a decrease of specific air consumption from 340—360 to 240—260 m^3/t [10].

Conclusions

For the design of new retorts for processing kukersite its following characteristics must be taken into account:

— tendency to bituminization of fine shale fractions on slow heating within the temperature range of 350—400 °C;

— presence of relatively large amounts of thermally unstable components among volatile products (e. g. oxygen compounds including high-boiling phenols) and predominance of calcium carbonate in the mineral part of oil shale;
— favourable effect of oil shale moisture on the yield of phenols including water-soluble alkyl resorcinols;
— relatively high specific heat consumption for kukersite thermal decomposition;
— relatively low mechanical and thermomechanical strength.
These unique properties of kukersite could be best used for oil production. High yields of phenol-rich oil including also water-soluble alkyl resorcinols can be achieved on retorting kukersite in the flow of oxygen-free gaseous heat carrier at a minimum possible partial pressure of oil vapours, without preliminary drying of oil shale, avoiding at the same time contacts between volatile products and the solid process residue containing free calcium oxide.

В. М. ЕФИМОВ, Т. А. ПУРРЕ

НЕКОТОРЫЕ ЗАКОНОМЕРНОСТИ, СПЕЦИФИЧЕСКИЕ СВОЙСТВА И ОСОБЕННОСТИ ПОЛУКОКСОВАНИЯ СЛАНЦА-КУКЕРСИТА

Резюме

К специфическим технологическим свойствам кукерсита, которые необходимо учитывать при создании агрегатов для термической переработки, относятся:
- сравнительно низкая механическая и термомеханическая прочность;
- битуминизация при медленном нагревании в пределах 350—400 °С, в первую очередь мелких фракций сланца;
- наличие в составе летучих продуктов сравнительно большого количества таких термически нестабильных компонентов, как кислородные соединения, в том числе высококипящей части фенолов, и преобладание в составе минеральной части сланца карбоната кальция;
- положительное влияние на выход фенолов, в том числе водорастворимых алкилрезорцинов, рабочей влаги сланца.

Наиболее полное использование уникальных свойств кукерсита обеспечивается при выработке смолы. Для получения высокого выхода смолы с повышенным содержанием фенолов, и в том числе водорастворимых алкилрезорцинов, характерных для продуктов полукоксования кукерсита, наиболее благоприятные условия достигаются при полукоксовании кукерсита в потоке газообразного теплоносителя с минимально возможным парциальным давлением паров смолы, без предварительной автономной подсушки сланца и желательно при полном исключении контакта летучих продуктов с твердым остатком переработки, содержащим свободный оксид кальция.

При необходимости же получения легких фракций смолы с небольшим содержанием фенолов (если эти фракции найдут квалифицированное использование), наоборот, необходимо обеспечить контакт летучих продуктов с твердым остатком переработки, содержащим как можно больше свободного оксида кальция. При этом желательна автономная подсушка сланца и использование для процесса твердого теплоносителя (таблица).

Естественно, при полукоксовании как кукерсита, так и горючих сланцев других месторождений должно быть соблюдено решающее условие, обеспечивающее возможность получения высокого выхода смолы: минимальным должно быть

абсолютное количество кислорода, поступающего в шахту полукоксования. Радикальным решением этой проблемы является, как известно из мировой практики, применение циркуляционного теплоносителя в слое. В случае переработки кускового сланца в генераторах равномерное распределение теплоносителя в слое наилучшим образом достигается при полукоксовании в кольцевой камере.

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Oil Shale Research Institute
Kohtla-Järve

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